

# PATENT ABSTRACTS OF JAPAN

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(71)Applicant : KANEKA CORP

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(72)Inventor : OKAMOTO TOSHIHIKO  
SAKAGUCHI MASAFUMI  
YUKIMOTO SADAO  
TAKASE JUNJI  
WAKABAYASHI KATSUO  
ANDO HIROSHI

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(54) CURABLE COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a curable composition giving a cured material which ensures practical curability and recovery properties and has mechanical properties including high strength and high elongation.

SOLUTION: The curable composition comprises (A) an organic polymer having at least one silicon-containing group which has a hydroxy group or a hydrolyzable group bonded to the silicon atom and which is crosslinkable by forming siloxane bonds, and (B) one or more sorts of metal carboxylates selected from calcium carboxylate, vanadium carboxylate, iron carboxylate, titanium carboxylate, potassium carboxylate, barium carboxylate, manganese carboxylate, nickel carboxylate, cobalt carboxylate and zirconium carboxylate.

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## CLAIMS

## [Claim(s)]

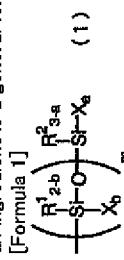
## [Claim 1]

(A) While containing an organic polymer and (B) carboxylic acid zirconium which have a hydroxyl group or a hydrolytic basis combined with a silicon atom, and have at least one silicon content group which can construct a bridge by forming a siloxane bond, it becomes considering an amine compound as an essential ingredient as a (C) ingredient.

(B) A hardenability constituent, wherein a carboxylic acid zirconium of an ingredient is a carboxylic acid zirconium in which the melting point has an acid radical of carboxylic acid which is 65 \*\* or less.

## [Claim 2]

(A) A number average molecular weight is within the limits of 500~50,000, and an organic polymer of an ingredient is a general formula to an end and/or a side chain of a main chain (1) :



(R<sup>1</sup> and R<sup>2</sup> among a formula) They are an alkyl group of the carbon numbers 1~20, an aryl group of the carbon numbers 6~20, an aralkyl group of the carbon numbers 7~20, or (R) SiO independently, respectively. — (R') respectively — independent — the substitution of the carbon numbers 1~20, or an unsubstituted hydrocarbon group — it is — it is the Tori ORGANO siloxy group shown. X is a hydroxyl group or a hydrolytic basis independently, respectively, as 0, 1, 2, or 3, b is 0, 1, or 2, and a and b are not simultaneously set to 0 m — the integer of 0, or 1~19 — it is — the hardenability constituent according to claim 1 having one or more hydrolytic silyl groups per molecule expressed.

## [Claim 3]

The hardenability constituent according to claim 2, wherein X is an alkoxy group.

## [Claim 4]

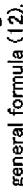
(A) A hardenability constituent in any 1 paragraph of Claims 1~3 whose organic polymers of an ingredient are a polyoxyalkylene series polymer and/or a saturated hydrocarbon system polymer.

## [Claim 5]

The hardenability constituent according to claim 4 which is a polymer, wherein said saturated hydrocarbon system polymer has a repeating unit resulting from isobutylene 50% of the weight or more in a total amount.

## [Claim 6]

(B) A hardenability constituent given in any 1 paragraph of Claims 1~5 to which a carboxylic acid zirconium of an ingredient uses as the main ingredients carboxylic acid metal salt expressed with a general formula (12).



(The inside R of a formula is substitution or an unsubstituted hydrocarbon group, and may include a carbon carbon double bond.)

## [Claim 7]

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## DETAILED DESCRIPTION

## [Detailed Description of the Invention]

## [Field of the Invention]

[0001]

In this invention, it has the hydroxyl group or hydrolytic basis combined with the silicon atom, and a siloxane bond is formed. Therefore, it is related with the hardenability constituent containing the organic polymer which has a silicon content group (henceforth a "reactive silicon group") which can construct a bridge.

## [Background of the Invention]

[0002]

It is known that the organic polymer which contains at least one reactive silicon group in a molecule has the interesting character in which construct a bridge by formation of the siloxane bond accompanied by the hydrolysis reaction of a reactive silicon group, etc., and a rubber-like hardened material is obtained with hygroscopic surface moisture etc. also in a room temperature.

[0003]

In the polymer which it has, these reactive silicon groups a polyoxyalkylene series polymer and a polyisobutylene system polymer, It is indicated by JP,S52-73998,A, JP,H5-125272,A, JP,H3-72527,A, JP,S63-6003,A, JP,S63-6041,A, JP,H1-38407,A. Especially a polyoxyalkylene series polymer and a polyisobutylene system polymer are already produced industrially, and are widely used for uses, such as a sealing material, adhesives, and a paint.

[0004]

When an organic polymer is a saturated hydrocarbon system polymer especially, since it excels in heat resistance, a water resisting property, weatherability, etc., if the hardened material obtained is used for a structural sealing material, the sealing material for multiple glass, etc., it is effective. The isobutylene system polymer which has a repeating unit which furthermore originates in isobutylene 50% of the weight or more in a total amount is preferred as a sealant aiming at moisture proof from especially the thing to excel in low moisture permeability and low gas permeability.

[0005]

Such a sealing material generally fills up the joined part and crevice between various members, the flatness nature to the use part ranging from being used to a long period of time in order to give watertight and airtightness becomes very important, and revealing sufficient elongation and intensity is called for.

[0006]

Amine compounds, such as lauryl amine, are used together as a co-catalyst in many cases for the purpose of a silanol condensation catalyst being used for bridge construction hardening of an organic polymer which, on the other hand, has such a reactive silicon group, and also accelerating a condensation reaction. As such a silanol condensation catalyst, divalent tin, such as octylic acid (2-ethylhexanoic acid) tin, The tin series catalyst represented by tetravalent tin, such as dibutyltin bisacetylectonate, is used widely, and when the movement of the part which places especially a sealing material is large, since the hardened material which has stability is obtained, many divalent tin is used.

[0007]

However, when octylic acid tin which is divalent tin, for example is used together with the amine compound of a co-catalyst and is used as a curing catalyst of the (A) ingredient, the intensity and elongation of a hardened material which are acquired may be insufficient, and an improvement of the further physical properties is desired.

[0008] Although most is a dibutyltin type, the latter tetravalent tin series catalyst being used now. While the hardened material obtained has emollient, i.e., having the character to follow to the long-term stress change from the outside and fast curability, it is broadly used from the ability to apply as a curing catalyst of 1 liquid mold-curing nature constituent. However, since toxicity in case a small amount of tributyltin contains in this is regarded as questionable, development of the silanol condensation catalyst of a non-tin series is desired.

[0009] In JP,S35-2795,B, JP,S32-3742,B, JP,S35-9839,B, JP,S37-3271,B, etc.. As a curing catalyst of an organopolysiloxane constituent, the carboxylic acid metal salt of various kinds of non-tin is indicated with carboxylate of tin. As an example in which the carboxylic acid metal salt of non-tin was used for the curing catalyst of the constituent which, on the other hand, contains the organic polymer which has a reactive silicon group. Although there were carboxylic acid bismuth (JP,H-39428,A, JP,H-12860,A) and carboxylic acid cerium (JP,2000-313814,A), there was no example broadly examined in various carboxylic acid metal salt until now.

[Patent documents 1] JP, S52-73998,A  
[Patent documents 2] JP,H5-125272,A  
[Patent documents 3] JP,H3-72527,A  
[Patent documents 4] JP,S33-6003,A  
[Patent documents 5] JP,S33-6041,A  
[Patent documents 6] JP,H1-38407,A  
[Patent documents 7] JP,H8-231758,A  
[Patent documents 8] JP,S35-2195,B  
[Patent documents 9] JP,S32-3742,B  
[Patent documents 10] JP,S35-9839,B  
[Patent documents 11] JP,S37-3271,B etc.  
[Patent documents 12] JP,H-39428,A  
[Patent documents 13] JP,H9-12860,A  
[Patent documents 14] JP,2000-313814,A  
[Description of the Invention]  
[Problem(s) to be Solved by the Invention]

[0010] The purpose of this invention is as follows. Have practical hardenability and stability with a good hardened material obtained. Provide a hardenability constituent useful as the structural sealing material asked especially for high durability, the sealing material for multiple glass, the moisture seal material used for an electric electronic component, adhesives, etc. from revealing the outstanding intensity and elongation.

## [Means for Solving the Problem]

[0011] In order that this invention persons may solve such a problem, as a result of inquiring, as a curing catalyst of the (A) ingredient Carboxylic acid calcium, Carboxylic acid vanadium, carboxylic acid iron, carboxylic acid titanium, carboxylic acid potassium. By using one or more sorts of carboxylic acid metal salt chosen from carboxylic acid barium, carboxylic acid manganese, carboxylic acid nickel, carboxylic acid cobalt, and a carboxylic acid zirconium. Securing moderate hardenability and stability, it finds out revealing high intensity and the physical properties of high elongation compared with a case where octylic acid tin is used as a curing catalyst, and came to complete this invention.

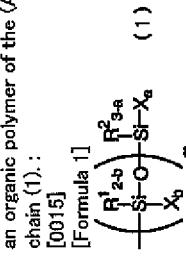
[0012] That is, this invention relates to an organic polymer which has a hydroxyl group or a hydrolytic basis combined with the (A) silicon atom, and has at least one silicon content group which can construct a bridge by forming a siloxane bond, and a hardenability constituent containing (B) carboxylic acid

zirconium.

[0013] An amine compound is related with the aforementioned hardenability constituent which becomes as an essential ingredient as a (C) ingredient.

[0014] As a desirable embodiment, a number average molecular weight is within the limits of 500–50,000, and an organic polymer of the (A) ingredient is a general formula to an end and/or a side chain of a main chain (1). :

[0015] [Formula 1]



[0016]

(R<sup>1</sup> and R<sup>2</sup> among a formula) They are an alkoy group of the carbon numbers 1–20, an aryl group of the carbon numbers 6–20, an aralkyl group of the carbon numbers 7–20, or (R')<sub>3</sub>SiO independently, respectively. — (R') respectively — independent — the substitution of the carbon numbers 1–20, or an unsubstituted hydrocarbon group — it is — it is the Tori ORGANOC siloxy group shown. X is a hydroxyl group or a hydrolytic basis independently, respectively, a is 0, 1, 2, or 3, b is 0, 1, or 2, and a and b are not simultaneously set to 0, m — the integer of 0, or 1–19 — it is — it is related with a hardenability constituent given in said either having one or more hydrolytic silyl groups per molecule expressed.

[0017] It is related with the aforementioned hardenability constituent characterized by X being an alkoy group as a desirable embodiment.

[0018] As a desirable embodiment, the organic polymer of the (A) ingredient is related with a hardenability constituent given in said either which is a polyoxyalkylene series polymer and/or a saturated hydrocarbon system polymer.

[0019] As a desirable embodiment, said saturated hydrocarbon system polymer is related with the aforementioned hardenability constituent which is a polymer having a repeating unit resulting from isobutylene 50% of the weight or more in a total amount.

[0020] As a desirable embodiment, a carboxylic acid zirconium of the (B) ingredient is related with a hardenability constituent given in said either which uses as the main ingredients carboxylic acid metal salt expressed with a general formula (12).

[0021]

(The inside R of a formula is substitution or an unsubstituted hydrocarbon group, and may include a carbon carbon double bond.) As a desirable embodiment, carboxylic acid metal salt of the (B) ingredient is related with a hardenability constituent given in said either which is the carboxylic acid metal salt in which the melting point has an acid radical of carboxylic acid which is 65 \*\* or less.

[0022] As a desirable embodiment, a carbon number in which carboxylic acid metal salt of the (B) ingredient contains carbon of a carbonyl group is related with a hardenability constituent given in said either which is the carboxylic acid metal salt which has an acid radical of carboxylic acid which is 2–17.

[0023] As a desirable embodiment, carboxylic acid metal salt of the (B) ingredient is related with a hardenability constituent given in said either which is metal salt of a carboxylic acid group content compound chosen from octylic acid, 2-ethylhexanoic acid, neo decanoic acid, oleo acid, or naphthenic acid.

[0024] It is related with a hardenability constituent given in said either containing the (B) ingredient of a quantity which serves as 0.005 – 5 weight section by metallic element conversion contained in the (B) ingredient to (A) ingredient 100 weight section as a desirable embodiment.

[0025] It is related with a hardenability constituent given in said either containing the (B) ingredient of a quantity which serves as 0.005 – 5 weight section by metallic element conversion contained in the (B) ingredient, the (C) ingredient 0.01 – 20 weight sections to (A) ingredient 100 weight section as a desirable embodiment.

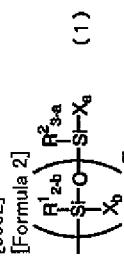
[Best Mode of Carrying Out the Invention]

[0026] Hereafter, this invention is explained in detail.

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[0031] As a reactive silicon group, it is a general formula (1).:

[0032]



siloxy group  $R^1$  is indicated to be by  ${}^3\text{SiO}$ —which is a methyl group, a phenyl group, etc. ( $R'$ , etc. are mentioned). In these, the point that the activity of a hydrolysis reaction is high to especially a methyl group is preferred.

[0042]

As more concrete illustration of a reactive silicon group, a trimethoxysilyl group, a triethoxysilyl group, a triisopropoxymethyl silyl group, a dimethoxymethyl silyl group, a diethoxymethylsilyl group, and a diisopropoxy methyl silyl group are mentioned. Its activity is high, and since especially the trimethoxysilyl group can reduce quantity of carboxylic acid metal salt, which is the (B), ingredient, it is preferred.

[0043]

What is necessary is just to perform introduction of a reactive silicon group by a publicly known method. That is, the following methods are mentioned, for example.

[0044]

(b) Make an organic compound which has an active group and an unsaturation group which show reactivity to an organic polymer which has functional groups, such as a hydroxyl group, in a molecule to this functional group react, and obtain an organic polymer containing an unsaturation group. Or an unsaturation group content organic polymer is obtained by copolymerization with an unsaturation group content epoxy compound. Subsequently, hydrosilane which has a reactive, silicon group is made to act on an acquired resultant, and it hydrolylates.

[0045]

(\*\*) Make a compound which has a sulphydryl group and a reactive silicon group react to an organic polymer containing an unsaturation group produced by making it be the same as that of the (b) method.

[0046]

(\*\*) Make a compound which has a functional group and a reactive silicon group which show reactivity to an organic polymer which has functional groups, such as a hydroxyl group, an epoxy group, and an isocyanate group, in a molecule to this functional group react.

[0047]

A method of making a compound which has a polymer, an isocyanate group, and a reactive silicon group which have a hydroxyl group react to an end a method of (b) or among (\*\*)'s from points, like a manufacturing cost becomes low in the above method is preferred.

[0048]

(b) As an example of a hydrosilane compound used in a method, For example, trichlorosilane, methylidichlorosilane, dimethylchlorosilane, Halogenation Silang like phenyl dichlorosilane; Trimethoxysilane,

[0049]

Triethoxysilane, methyl diethoxysilane, The alkoxysilane like phenyl diacetoxysilane; although dimethoxysilane; Methylidic acetoxy silane, The acyloxy silanes like a phenyldiacetoxysilane; although the KE TOKISHI mate silanes like bis(dimethyl KETOKISHI mate)methyl dimethoxysilane and bis(cyclohexyl KETOKISHI mate)methyl dimethoxysilane are raised, it is not limited to these. Among these, halogenation Silang and alkoxy silane are especially preferred from points, like availability and hydrolysis reaction nature are high.

[0050]

(\*\*) Although a method of introducing into an unsaturation binding site of an organic polymer a compound which has a sulphydryl group and a reactive silicon group as a synthetic method by a radical addition reaction under a radical initiator and/or radical source-of-release existence, for example, etc. are mentioned, it is not limited in particular. As an example of a compound of having said sulphydryl group and a reactive silicon group. For example, although gamma-mercaptopropyl propyltrimethoxysilane, gamma-mercaptopropylmethyl dimethoxysilane, gamma-mercaptopropyl triethoxysilane, gamma-mercaptopropylmethyl diethoxysilane, etc. are raised, it is not limited to these.

[0051]

(\*\*) Although a method etc. which are shown in JP,H3-47825,A are mentioned, for example as a method of making a compound which has a polymer, an isocyanate group, and a reactive silicon group which have a hydroxyl group reacting to an end among synthetic methods, it is not limited in particular. As an example of a compound of having said isocyanate group and a reactive silicon group, For example, although gamma-isocyanate propyltrimethoxysilane, gamma-isocyanate propylmethoxysilane, gamma-mercaptopropylmethyl diethoxysilane, etc. are raised, it is not limited to these.

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dimethoxysilane, gamma-isocyanatepropyl triethoxysilane, gamma-isocyanate propylmethyl diethoxysilane, etc. are raised. It is not limited to these.

[0051]

As for a silane compound which three hydrolytic bases have combined with one silicon atoms, such as trimethoxysilane, disproportionation may advance. If disproportionation progresses, a remarkable dangerous compound [like ] which is dimethoxysilane will arise. However, such disproportionation advances in neither gamma-mercaptopropyltrimethoxysilane nor gamma-isocyanate propyltrimethoxysilane. For this reason, when three hydrolytic bases, such as trimethoxysilyl group, use a basis combined with one silicon atom as a silicon content group, it is preferred to use a synthetic method of (\*\*) or (\*\*).

[0052]

(A) A number average molecular weight of an organic polymer which is an ingredient, In polystyrene conversion in GPC (gel permeation chromatography), it is preferred that it is 500 to about 50,000, and about 1,000 to 30,000 liquefied thing which is, carries out and has mobility is especially preferred from points, such as the ease of dealing with it. If sufficient rubber elasticity is not obtained and 50,000 is exceeded when a number average molecular weight is less than 500, since it is lacking in mobility and handling is difficult for it, at ordinary temperature, it is not desirable.

[0053]

(A) A reactive silicon group in one molecule of organic polymers which are an ingredient is one or more pieces, and it is preferred that there are 1.1~5 pieces. Since it will become weak firmly and will become scarce at rubber elasticity if hardenability becomes insufficient, good rubber elasticity may not longer be obtained, if the number of reactive silicon groups contained in a molecule will be less than one piece, and five pieces are exceeded, it is not desirable.

[0054]

A reactive silicon group may be in a main chain terminal or a side chain of an organic polymer, and may be in both. Since effective network chain density of an organic polymer component contained in a hardened material formed eventually increases especially when a reactive silicon group is in a main chain terminal, it is desirable from points, like a rubber-like hardened material of high elongation becomes is easy to be obtained with high intensity.

[0055]

Said polyoxyalkylene series polymer is a general formula intrinsically (14).:

[0056]

[Formula 4]



kind of repeating unit, and may consist of two or more kinds of repeating units. When used especially for sealant etc., it is desirable from that what comprises the polymer which uses a polyoxypropylene system polymer as the main ingredients is amorphous, or the point which is hypoviscosity comparatively.

[0060]

As a synthetic method of a polyoxyalkylene series polymer, For example, the polymerizing method by an alkali catalyst like KOH, the polymerizing method by a transition metal compound-porphyrin complex catalyst [like a complex produced by making an organoaluminum compound and porphyrin which are shown in JP,61-215623,A react, JP,46-27250,B, JP,59-15336,B, a U.S. Pat. No. 3278457 item, a U.S. Pat. No. 3278458 item, A U.S. Pat. No. 3278459 item, a U.S. Pat. No. 3421256 item, a U.S. Pat. No. 3427334 item, The polymerizing method by a composite metal cyanide complex catalyst shown in a U.S. Pat. No. 3427335 item etc., \*\*\*\*\* such as the polymerizing method using a catalyst which consists of a polyphosphazene salt illustrated by JP,H10-273512,A, and the polymerizing method using a catalyst which consists of a phosphazene compound illustrated by JP,H11-060722,A, are not limited in particular.

[0061]

In a principal chain skeleton of the above-mentioned polyoxyalkylene series polymer, other ingredients, such as a urethane bond ingredient, may be included in the range which does not spoil an effect of this invention greatly.

[0062]

It is not limited especially as the above-mentioned urethane bond ingredient, but For example, tolylene diisocyanate, Aromatic system polyisocyanates, such as diphenylmethane diisocyanate and xylylene diisocyanate; Isophorone diisocyanate, What is obtained from a reaction of polyisocyanate compounds, such as aliphatic series system polyisocyanates, such as hexamethylene di-isocyanate, and polyol which has a repeating unit of the above-mentioned general formula (14) can be mentioned.

[0063]

[0063] A manufacturing method of a polyoxyalkylene series polymer which has a reactive silicon group, JP,45-36319,B, JP,46-12154,B, JP,50-156599,A, JP,54-6096,A, JP,55-13767,A, JP,56-13468,A, JP,57-64123,A, JP,3-2450,B, a U.S. Pat. No. 3632557 item, What is proposed by each gazette, such as a U.S. Pat. No. 4345053 item, a U.S. Pat. No. 4366307 item, and a U.S. Pat. No. 4960844 item, JP,61-197631,A, JP,61-215622,A, JP,61-215623,A, JP,61-218632,A, JP,H3-72527,A, JP,H3-47825,A, Although it is indicated by each gazette of JP,H8-231707,A and 6,000 or more number average molecular weights and Mw/Mn (ratio of weight average molecular weight and a number average molecular weight) can use conveniently a polyoxyalkylene series polymer with narrow molecular weight distribution in the 1.8 or less amount of Polymer Division, It is not limited to in particular these.

[0064]

A polyoxyalkylene series polymer which has the above-mentioned reactive silicon group may be used alone, and may be used together two or more sorts.

[0065]

A polymer which makes a skeleton of a saturated hydrocarbon system polymer which has a reactive silicon group used for this invention, (1) [ whether an olefinic compound of the carbon numbers 1~6, such as ethylene, propylene, 1-butene, and isobutylene, is polymerized as the main ingredients, and ] (2) After making diene series, such as butadiene and isoprene, homopolymerize or carrying out copolymerization to the above-mentioned olefinic compound, can obtain by a method of hydrogenating, but, Since an isobutylene system polymer and a hydrogenation polybutadiene system polymer tend to introduce a functional group into an end, and tend to control a molecular weight and can increase the number of end functional groups, they are preferred.

[0066]

All the monomeric units may be formed from an isobutylene unit, and an isobutylene system polymer, It is [ in an isobutylene system polymer ] desirable, and a monomeric unit which has isobutylene and copolymeric may be especially contained in 10 or less % of the weight of the range preferably 30 or less % of the weight still more preferably 50 or less % of the weight. In an isobutylene system polymer, when content of a monomeric unit which has isobutylene and copolymeric exceeds 50 % of the



[0059] \*\* is mentioned. The principal chain skeleton of a polyoxyalkylene series polymer may consist of one

weight, since characteristic physical properties, such as high weatherability, high heat resistance, low moisture permeability, etc. resulting from an isobutylene skeleton, are not fully revealed, it is not desirable.

[0067] As such a monomer component, an olefin of the carbon numbers 4–12, vinyl ether, an aromatic vinyl compound, vinylsilane, and arylsilane are raised, for example. As such a copolymer component, for example 1-butene, 2-butene, A, 2-methyl-1-butene, a pentene, 4-methyl-1-pentene, alpha-methylstyrene, a vinylcyclohexene, dimethylstyrene, Monochlorostyrene, dichlorostyrene, beta-pinene, indene, vinyl trichlorosilane, Vinyl methylchlorosilane, vinylidemethylchlorosilane, vinyltrimethylmethoxysilane, Vinyl trimethylsilane, divinyl dichlorosilane, divinyl dimethoxysilane, Divinyl dimethylsilane, the 1,3-divinyl-1,1, and 3,3-tetramethyl disiloxane, TORIBI nitrile methylsilane, a tetravinyl silane, allyltriethylchlorosilane, Allyl trimethyl chlorosilane, diaryl dimethoxy silane, diaryl dimethyl methoxysilane, allyl dichlorosilane, diaryl dimethoxysilane, gamma-methacryloyl oxypropyl methyl dimethoxysilane etc. are raised.

[0068] As a monomeric unit which has isobutylene and copolymeric among the above, if vinylsilane and arylsilane are used, a basis which silicon content increases and can act as a silane coupling agent will increase, and the adhesive property of a constituent obtained will improve.

[0069] Other monomeric units may be made to contain besides a monomeric unit used as the main ingredients like a case of the above-mentioned isobutylene system polymer in a hydroxylation polybutadiene system polymer or other saturated hydrocarbon system polymers.

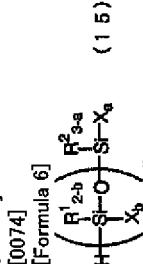
[0070] To a saturated hydrocarbon system polymer which has a reactive silicon group used for this invention. A little monomeric units in which an after-polymerization double bond like polyene compounds, such as butadiene and isoprene, remains in the range in which the purpose of this invention is attained may be made to contain in 1 or less % of the weight of the range preferably especially 5 or less % of the weight still more preferably 10 or less % of the weight.

[0071] A saturated hydrocarbon system polymer which has these reactive silicon groups can be independent, or can be used together two or more sorts.

[0072] A process of a saturated hydrocarbon system polymer which has a reactive silicon group next is explained.

[0073] An isobutylene system polymer which has a reactive silicon group in molecular chain terminals among isobutylene system polymers which have a reactive silicon group, an end organic-functions type obtained by the polymerizing method (cationic polymerization method using a specific compound combining and [ which is called iniphor ] and a chain transfer agent) called iniphor method — it can manufacture preferably using a whole end organic-functions type isobutylene system polymer. As a process of a saturated hydrocarbon system polymer which has a reactive silicon group. For example, general formula (15) after obtaining polyisobutylene which has an unsaturation group at the end by dehydrohalogenation reaction of an end of a polymer which has third class carbon-chlorine combination obtained by a polymerization reaction, the reaction of an end of a polymer and allyl trimethylsilane which have third class carbon-chlorine combination, etc. :

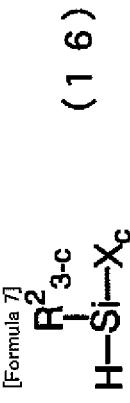
[0074] [Formula 6]



(R<sup>1</sup>, R<sup>2</sup>, X, m, a, and b are the same as the above among a formula.) — the hydrosilane compound (this compound is a compound which the hydrogen atom combined with the basis expressed with a general formula (11)) expressed — desirable — general formula (16):

[0075] (R<sup>1</sup>, R<sup>2</sup>, X, m, a, and b are the same as the above among a formula.) — the hydrosilane compound (this compound is a compound which the hydrogen atom combined with the basis expressed with a general formula (11)) expressed — desirable — general formula (16):

[0076] [Formula 7]



[0077] (R<sup>2</sup>, X, and c are the same as the above among a formula.) — it can obtain by the reaction (hydroxilation reaction) to which the hydrosilane compound expressed is made to add using a platinum catalyst.

[0078] As a hydrosilane compound, for example Trichlorosilane, methylid chlorosilane, Halogenation Silang like dimethylchlorosilane and phenyl dichlorosilane, Trimethoxysilane, Triethoxysilane, methyldiethoxysilane, methyl dimethoxysilane, The alkoxysilane like phenyl dimethoxysilane; Methyldi acetoxy silane, The acyloxy silanes like a phenyldiacetoxy silane; although the KETOKISHI mate silanes like bis(dimethyl KETOKISHI mate)methylsilane and bis(cyclohexyl KETOKISHI mate)methylsilane are raised, it is not limited to these. Among these, halogenation Silang and alkoxy silane are preferred especially in respect of the ease of acquisition, etc.

[0079] Such a manufacturing method is indicated in each gazette of JP-4-69659,B, JP,7-108928,B, JP,63-254145,A, JP,64-22304,A, and the patent No. 2539445, for example.

[0080] An isobutylene system polymer which has a reactive silicon group in a chain side chain is manufactured by adding and carrying out copolymerization of the vinylsilane and arylsilane which have a reactive silicon group into a monomer containing isobutylene.

[0081] In the case of a polymerization reaction which manufactures an isobutylene system polymer which has a reactive silicon group in molecular chain terminals. After carrying out copolymerization of the vinylsilane and arylsilane etc. which have a reactive silicon group in addition to an isobutylene monomer which is the main ingredients, an isobutylene system polymer which has a reactive silicon group in an end and a chain side chain is manufactured by introducing a reactive silicon group into an end.

[0082] As the vinylsilane which has a reactive silicon group, and arylsilane, For example, vinyl trichlorosilane, vinyl methylid chlorosilane, vinyldimethylchlorosilane, Vinylidimethylmethoxysilane, divinyldichlorosilane, divinyl dimethoxysilane, Allylchlorosilane, allyl methylid chlorosilane, allylidimethylchlorosilane, Allyldimethyl methoxysilane, diaryl dichlorosilane, diaryl dimethoxysilane, gamma-methacryloyl oxypropyl methyl dimethoxysilane, etc. are raised.

[0083] In this invention, a hydrogenation polybutadiene polymerization object which has a reactive silicon group can be mentioned as a saturated hydrocarbon system polymer which has a reactive silicon group. A hydrogenation polybutadiene polymerization object which has a reactive silicon group can be acquired by the hydrosilylation reaction of a hydrogenation polybutadiene system polymer which has an olefin group. General formula (17) after a hydrogenation polybutadiene system polymer which has an end hydroxyl group uses a hydroxyl group of an end hydroxy hydrogenation polybutadiene system polymer as oxy metal groups, such as -ONa and -OK, first, for example :

$\text{CH}_2=\text{CH}-\text{R}^4-\text{Y}$  (17)

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Halogen atoms, such as a chlorine atom, a bromine atom, and iodine atoms, and R<sup>4</sup> are among type, and Y is -R<sup>5</sup>, -R<sup>5</sup>-OCO-, or -R<sup>5</sup>-CO-. (R<sup>5</sup> is a divalent hydrocarbon group of the carbon numbers 1-20, and) an alkylene group, a cyclo-alkylene group, an allylene group, and an aralkylene group — it is desirable — by a divalent organic group shown. — It can obtain by making an organic halogenated compound shown by especially a divalent basis chosen from CH<sub>2</sub><sup>-</sup> and -R<sup>4</sup>-C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub><sup>-</sup> (R<sup>4</sup> is a hydrocarbon group of the carbon numbers 1-10) being preferred] react.

[0084] As a method of using terminal hydroxyl groups of an end hydroxy hydrogenation polybutadiene system polymer as a oxy metal group, A method of making it react to alkaline-water oxides, such as Na, metal alkoxide;NaOH like metal hydride;NaOCH<sub>3</sub> like alkaline metal;NaH like K, and KOH, etc. is raised

**[0085]** Although an end olefin hydrogenation polybutadiene system polymer with the almost same molecular weight as an end hydroxy hydrogenation polybutadiene system polymer used as a starting material is obtained in said method, Before making an organic halogenated compound of a general formula (17) react to obtain a polymer of the amount of Polymer Division more, at the time, such as a methylene chloride, bis(chloromethyl)benzene, and bis(chloromethyl)ether. If it is made to react to an organic halogenated compound which can increase a molecular weight if it is made to react to a multivalent organic halogenated compound which contains two or more halogen in one molecule, and is shown by a general formula (17) after that, A hydrogenation polybutadiene system polymer which is the amount of Polymer Division more, and has an olefin group at the end can be obtained.

**[Footnote]** As an example of an organic halogenated compound shown by said general formula (17). For example, an allyl chloride, an allyl star's picture, vinyl(chloromethyl) benzene, Allyl(chloromethyl) benzene, allyl (bromomethyl) benzene. Although allyl (chloromethyl) ether, allyl(chloromethoxy) benzene, 1-buteneyl (chloromethyl) ether, 1-hexenyl(chloromethoxy) benzene, allyloxy (chloromethyl) benzene, etc. are raised, it is not limited to them. Among these, an allyl chloride is cheap, and since it moreover reacts considerably, it is preferable.

[0087] Introduction of a reactive silicon group to said olefin hydrogenation polybutadiene system polymer may be manufactured by carrying out an addition reaction using a platinum system catalyst in a hydrosilane compound like a case of an isobutylene system polymer which has a reactive silicon

[Q088] When a saturated hydrocarbon system polymer which has a reactive silicon group as mentioned above does not contain substantially an unsaturated bond which is not an aromatic ring in a molecule compared with a sealing agent etc. which consist of a conventional rubber system polymer like an organic system polymer or an oxyalkylene system polymer which has an unsaturated bond, weatherability becomes good remarkably. Since this polymer is a hydrocarbon system polymer, its weatherability becomes good remarkably. Since this polymer is a hydrocarbon system polymer, its weatherability becomes good remarkably. Since this polymer is a hydrocarbon system polymer, its weatherability becomes good remarkably.

An organic polymer which has these reactive silicon groups may be used alone, and may be used together two or more sorts. Specifically, a polyoxyalkylene series polymer which has a reactive silicon group, a saturated hydrocarbon system polymer which has a reactive silicon group, a vinyl-base polymer which has a reactive silicon group, and an organic polymer which blends two or more sorts

**[0090]** A manufacturing method of an organic polymer which blends a polyoxyalkylene series polymer which has a reactive silicon group, and a vinyl-l-base polymer which has a reactive silicon group. Although indicated by JP,59-122541,A, JP,63-112642,A, JP,H6-172931,A, JP,H11-116763,A, etc., it is not chosen from a group, ~~and~~, and other s, can also be used.

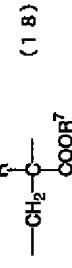
limited to in particular these.

Adujunctive elements

N. J. GOLDBECK

[0092] *Journal of Oral Rehabilitation* 2005; 32: 200–205

[Formula 8]



100003

[0933] the acrylic ester monomer unit which has an alkyl group of the carbon numbers 1-8 expressed with the acrylic ester monomer unit which has an alkyl group of the carbon numbers 1-8 expressed with hydrogen atom or a methyl group, and R<sup>7</sup> show the alkyl group of the carbon numbers 1-8 among a formula as for R<sup>5</sup> (methyl) and following general formula (19).

[0094]

(19)

[0095] --- the inside of a formula, and R<sup>6</sup> --- the above --- the same --- R<sup>8</sup> shows a with a carbon numbers of ten or more alkyl group --- to the copolymer which consists of an acrylic ester monomer unit which has with a carbon numbers of ten or more expressed alkyl group (meta-). It is the method of blending and manufacturing the polyoxalkylene series polymer which has a reactive silicon group. Acrylic acid (meta) expresses acrylic acid and/or methacrylic acid with the above-mentioned

[0096] as R<sup>7</sup> of said general formula (18) — the carbon numbers 1-8 of a methyl group, an ethyl group, a propyl group, n-butyl group, t-butyl group, etc. — desirable — 1-4 — an alkyl expressive form.

group of 1-2 is raised still more preferably. An alkyl group of R<sup>7</sup> may be independent and may be

as  $R^8$  of said general formula (19) — ten or more carbon numbers of a lauryl group, a tridecyl group, a cetyl group, a stearyl group, a behenyl group, etc. — usually — 10-30 — a long-chain alkyl group of 10-20 is raised preferably. Like a case of  $R^7$ , an alkyl group of  $R^8$  may be independent and may be

[0098] Although a chain of this vinyl system copolymer consists of a monomeric unit of a formula (18) and formula (19), substantially, a "real target" here means that the sum total of a monomeric unit of a formula (18) which exists in this copolymer, and a formula (19) surpasses 50 % of the weight. The sum total of a monomeric unit of a formula (18) and a formula (19) is 70 % of the weight or more.

[0099] From a point of compatibility with a polyoxyethylene series polymer, as for an abundance ratio of a monomeric unit of a formula (18), and a monomeric unit of a formula (19), 95.5-40.60 are preferred as a preference.

As monomeric units other than a formula (18) which may be contained in this copolymer, and a formula (19). For example, carboxylic acid groups, such as acrylic acid and methacrylic acid, acrylamide, Amide groups, such as methacrylamide, N-methylacrylamide, and N-methyloxymethacrylamide, Epoxy groups, such as glycidyl acrylate and glycidyl methacrylate, Diethylamino ethyl acrylate, diethylamino ethyl methacrylate, A monomer containing amino groups, such as aminooethyl vinyl ether, a monomeric unit which originates in acrylonitrile, styrene, alpha-methylstyrene, alkyl vinyl ether, VCM/PVC, vinyl acetate, vinyl propionate, ethylene, etc. in addition a weight ratio, and 90:10-60:40 are still more preferred.

2010/05/06

[0101]

Although an organic polymer which blends a saturated hydrocarbon system polymer which has a reactive silicon group, and a vinyl-base polymer which has a reactive silicon group is indicated by JP,H1-168764,A, JP,2006-188176,A, etc., it is not limited to in particular these.

[0102] A method of polymerizing an acrylic ester (meta) system monomer elsewhere under existence of an organic polymer which has a reactive silicon group as a manufacturing method of an organic polymer which blends a vinyl-base polymer which has a reactive silicon group can be used. Although this manufacturing method is concretely indicated by each gazette, such as JP,59-78223,A, JP,59-168014,A, JP,60-228516,A, and JP,60-228517,A, it is not limited to these.

[0103]

Carboxylic acid calcium used as a (B) ingredient in a hardenability constituent of this invention, Carboxylic acid vanadium, carboxylic acid iron, carboxylic acid potassium, carboxylic acid titanium, carboxylic acid manganese, and a carboxylic acid zirconium may be made to form from a silanol condensation catalyst in which a silicon atom contained in an organic polymer which is the (A) ingredient of this invention, or a hydrolytic basis.

[0104]

In said carboxylic acid metal salt, carboxylic acid calcium, carboxylic acid vanadium, carboxylic acid iron, carboxylic acid titanium, carboxylic acid potassium, carboxylic acid barium, carboxylic acid manganese, and a carboxylic acid cobalt, and a carboxylic acid cobalt, and a carboxylic acid zirconium, It is more desirable from a point that the activity of a catalyst is high, carboxylic acid calcium, carboxylic acid iron, carboxylic acid titanium, and a carboxylic acid zirconium are still more preferred, and carboxylic acid iron and carboxylic acid titanium are especially the most preferred.

[0105]

Carboxylic acid calcium, carboxylic acid vanadium, carboxylic acid titanium, carboxylic acid potassium, carboxylic acid barium, carboxylic acid nickel, carboxylic acid cobalt, and a carboxylic acid zirconium, It is more desirable from a point with little coloring of a hardenability constituent obtained, and a point that the heat resistance of a hardened material and weatherability which are obtained are high, and carboxylic acid calcium, carboxylic acid titanium, carboxylic acid potassium, carboxylic acid barium, and a carboxylic acid zirconium are still more preferred.

[0106]

This (B) ingredient uses as the main ingredients carboxylic acid metal salt expressed with general formula (2) - (12), respectively.

 $\text{Ca}(\text{OCOR})_2$  (2) $\text{V}(\text{OCOR})_3$  (3) $\text{Fe}(\text{OCOR})_2$  (4) $\text{Fe}(\text{OCOR})_3$  (5) $\text{Ti}(\text{OCOR})_4$  (6) $\text{K}(\text{OCOR})_7$  $\text{Ba}(\text{OCOR})_2$  (8) $\text{Mg}(\text{OCOR})_2$  (9) $\text{nickel}(\text{OCOR})_2$  (10) $\text{Co}(\text{OCOR})_2$  (11) $\text{Zr}(\text{O}) (\text{OCOR})_2$  (12)

(The inside R of a formula is substitution or an unsubstituted hydrocarbon group, and may include a carbon carbon double bond.)  
As carboxylic acid, a carboxylic acid group content compound of a hydrocarbon system of 2-40 is used suitably, and a carbon number including carbonyl carbons may be especially used for a carboxylic acid group content compound of a hydrocarbon system of the carbon numbers 2-20

suitably from a point of availability here.

[0107]

When it illustrates concretely, acetoic acid, propionic acid, butanoic acid, a valeric acid, caproic acid, lauric acid, tridecylacid, myristic acid, pentadecyl acid, Palmitic acid heptadecylacid, stearic acid, nonadecanoic acid, arachin acid, Behenic acid, lignoceric acid, cerinic acid, undecenoic acid, melissic acid, Straight chain saturated fatty acid groups, such as RAJUSERU acid, Undecenoic acid, Linder acid, Tsuzuic acid, FIZETERIN acid, myristoleic acid, 2-hexadecenoic acid, 6-hexadecenoic acid, 7-hexadecenoic acid, palmoleic acid, a petroselinic acid, Monoeno unsaturations, such as oleic acid, elaidic acid, ASUKUREPIN acid, vaccenic acid, erodoleic acid, Gondo Inra acid, a ceteoleic acid, erucic acid, brassidic acid, selacholeic acid, KISHIMEN acid, and RUMEKUEN acid

Fatty acid; Linolic acid, 10,12-octadecadienoic acid, HIRAGO acid, Alpha-eleostearic acid, beta-eleosteric acid, punctic acid, linolenic acid, 8,11,14-eicosatrienoic acid, a 7,10,13-docosatrienoic acid, 4,8,11,14-hexadeca tetraenoic acid, MORUCHI acid, ster RIDON acid, Arachidonic acid, 8,12,16,19-docosatetraenoic acid, 4,8,12,15,18-eicosapentaenoic acid, Polyene unsaturated fatty acid, such as clupanodonic acid, herring acid, and docosahexaenoic acid; Iso acid, Branch fatty acid, such as anteiso acid, tuberculostearic acid, a pivalic acid, and neo decanoic acid; A tartric acid, Fatty acid with triple bonds, such as steer roll acid, a crepenylic acid, KISHIMEN acid, and 7-hexa crepe-de-Chine acid; Naphthenic acid, A malvalic acid, stericulic acid, HIDONO carbyne acid, chaulmoogric acid, Alicyclic carvone acids, such as geranic acid; Sabinic acid, 2-hydroxytetradecanoic acid, IPURORU acid, 2-hydroxyhexadecanoic acid, YARAPI Narian acid, uni-PERIN acid, AMBURETTORU acid, ARYURITTO acid, 2-hydroxyoctadecanoic acid, 12-hydroxyoctadecanoic acid, 9,10-dihydroxyoctadecanoic acid, Oxygenated fatty acid, such as ricinoleic acid, cam ROREN acid, licanic acid, farron acid, and cerebronic acid, such as succinic acid, glutaric acid, adipic acid, pimelic acid, SUPERIN acid, azelaic acid, and sebacic acid, is mentioned.

[0108]

when the melting point of said carboxylic acid is high (crystallinity is high), the melting point becomes high in a similar manner, and it is hard to deal with carboxylic acid metal salt which has the acid radical (workability — bad). Therefore, as for the melting point of said carboxylic acid, it is preferred that it is 65 \*\* or less, it is more preferred that it is -50-50 \*\*, and it is preferred that it is especially -40-35 \*\*.

[0109]

when a carbon number of said carboxylic acid is large (a molecular weight is large), it becomes liquefied and carboxylic acid metal salt which has the acid radical becomes a thing which has a high solid state or viscosity and which is hard to deal with it (workability — bad). On the contrary, when a carbon number of said carboxylic acid is small (a molecular weight is small), catalyst ability of carboxylic acid metal salt may fall [ carboxylic acid metal salt which has the acid radical ], including mostly an ingredient which volatilizes easily with heating. Especially on conditions (thin layer) which extended a constituent thinly, volatilization by heating may be large and catalyst ability of carboxylic acid metal salt may fall greatly. Therefore, as for said carboxylic acid, it is preferred that carbon numbers including carbon of a carbonyl group are 2-17, it is more preferred that it is 3-13, and it is preferred that it is especially 5-10.

[0110]

Especially acquisition is easy, and is cheap and a point that compatibility with the (A) ingredient is good to said carboxylic acid has 2-ethylhexanoic acid, octylic acid, neo decanoic acid, oleic acid, or preferred naphthenic acid. Said naphthenic acid is expressed with an empirical formula (20).

 $\text{CnH}_{2n-2}\text{O}_2$  (20)

carboxylic acid (2-ethylhexanoic acid etc.), whose carbon atoms in which said carboxylic acid adjoins a carbonyl group are the third class carbon and carboxylic acid (neo decanoic acid), which is quaternary carbon A pivalic acid etc. are more preferred from a cure rate being quick, and especially carboxylic acid whose carbon atom which adjoins a carbonyl group is quaternary carbon is preferred.

[0111]

From a viewpoint of availability and compatibility, as an example of desirable carboxylic acid metal salt, 2-ethylhexanoic acid iron (divalent), 2-ethylhexanoic acid iron (trivalent), 2-ethylhexanoic acid

titanium (tetravalence), 2-ethylhexanoic acid vanadium (trivalent), 2-ethylhexanoic acid calcium (divalent), 2-ethylhexanoic acid potassium (univalent), 2-ethylhexanoic acid barium (divalent), 2-ethylhexanoic acid manganese (divalent), 2-ethylhexanoic acid nickel (divalent), 2-ethylhexanoic acid cobalt (divalent), 2-ethylhexanoic acid zirconium (tetravalence), neo decanoic acid iron (trivalent), neo decanoic acid titanium (tetravalence), neo decanoic acid vanadium (trivalent), neo decanoic acid calcium (divalent), neo decanoic acid potassium (univalent), neo decanoic acid barium (divalent), a neo decanoic acid zirconium (tetravalence). Oleic acid iron (divalent), oleic acid calcium (divalent), oleic acid potassium (univalent), Oleic acid barium (trivalent), manganese oleate (divalent), oleic acid nickel (divalent), Oleic acid cobalt (divalent), an oleic acid zirconium (tetravalence), naphthenic acid iron (trivalent), Naphthenic acid iron (trivalent), naphthenic acid titanium (tetravalence), naphthenic acid vanadium (trivalent), Calcium naphthenate (divalent), naphthenic acid potassium (univalent), naphthenic acid barium (divalent), manganese naphthenate (divalent), naphthenic acid nickel (divalent), cobalt naphthenate (divalent), a naphthenic acid zirconium (tetravalence), etc. are mentioned.

[0112] 2-ethylhexanoic acid iron (divalent) from a viewpoint of catalytic activity, 2-ethylhexanoic acid iron (trivalent), 2-ethylhexanoic acid titanium (tetravalence), neo decanoic acid iron (divalent), Neo decanoic acid iron (trivalent), neo decanoic acid titanium (tetravalence), oleic acid iron (divalent), Oleic acid iron (trivalent), oleic acid titanium (tetravalence), naphthenic acid iron (divalent), Naphthenic acid iron (trivalent) and naphthenic acid titanium (tetravalence) are more preferred, and 2-ethylhexanoic acid iron (trivalent), neo decanoic acid iron (trivalent), oleic acid iron (trivalent), and especially naphthenic acid iron (trivalent) are preferred.

[0113] From a viewpoint of coloring to 2-ethylhexanoic acid titanium (tetravalence), 2-ethylhexanoic acid calcium (divalent), 2-ethylhexanoic acid potassium (univalent), 2-ethylhexanoic acid barium (divalent), 2-ethylhexanoic acid zirconium (tetravalence), Neo decanoic acid titanium (tetravalence), neo decanoic acid calcium (divalent), Neo decanoic acid zirconium (tetravalence), Oleic acid titanium (tetravalence), oleo acid (divalent), a neo decanoic acid zirconium (tetravalence), Oleic acid barium (divalent), an oleic acid calcium (divalent), oleic acid potassium (univalent), Oleic acid barium (divalent), naphthenic acid titanium (tetravalence), naphthenic acid barium (divalent), calcium naphthenate (divalent), naphthenic acid potassium (univalent), naphthenic acid barium (divalent), and a naphthenic acid zirconium (tetravalence) are more preferred.

[0114] Such carboxylic acid metal salt makes a carboxylic acid group content compound, or its ester and sodium hydroxide react, and makes solution of hard soap. Solution of metal salt prepared apart from this in addition, a sedimentation method which settles metallic soap, A carboxylic acid group content compound or its ester and metalated hydroxide, an oxide, A method etc. to which an alcoholate or a chloride, and a carboxylic acid group content compound are made to react in [ ] else /, such as scorchification to which a weak acid salt is made to react at an elevated temperature, and direct method to which a carboxylic acid group content compound and metal powder are made to react, ] an anhydrous organic solvent are taken.

[0115] As for such carboxylic acid metal salt, it is preferred to dilute with diluting solvents, such as a mineral spirit, toluene, hexylene glycol, a diethylene glycol, a paraffin oil, and diethyl phthalate, and to be used with a gestalt of a solution whose metal content is about 1 to 40 % of the weight.

[0116] (B) About 0.005-5 weight sections are preferred at metallic element conversion contained in the (B) ingredient to (A) ingredient 100 weight section as amount of ingredient used, and also about 0.01-3 weight sections are preferred. (B) Since a cure rate may become slow and a hardening reaction will become fully difficult to advance if loadings of an ingredient are less than this range, it is not desirable. On the other hand, pot life becomes short too much and is not preferred from a point of workability except that a good hardened material will become generation of heat and foaming local at the time of hardening arise, and is hard to be obtained, if loadings of the (B) ingredient exceed this range.

[0117]

The aforementioned carboxylic acid calcium, carboxylic acid vanadium, carboxylic acid iron, carboxylic acid titanium, carboxylic acid potassium, carboxylic acid barium, carboxylic acid manganese, carboxylic acid nickel, carboxylic acid cobalt, and a carboxylic acid zirconium. Besides using it alone, it can be used combining two or more sorts, and also can use together with carboxylic acid tin salt, carboxylic acid bismuth salt, carboxylic acid cerio salt, etc.

[0118] On the other hand, only with carboxylic acid metal salt of the (B) ingredient, activity is low, and when moderate hardenability is not acquired, various amine compounds which are the (C) ingredients as a co-catalyst can be added. As various amine compounds, although indicated to JP H5-287187,A, for example, Specifically Methylamine, ethylamine, propylamine, isopropylamine, A butylamine, amyl amine, hexylamine, octylamine, 2-ethylhexylamine, Nonyl amine, decyl amine, lauryl amine, pentadecyl amine, Aliphatic series primary amines, such as Sept Iles amine, stearylamine, and cyclohexylamine. Dimethylamine, Diethylamine, Dipropyl amine, diisopropyl amine, dibutyl amine, diamyl amine, di(2-ethylhexyl) amine, didecyl amine, diisobutyl amine, triethylamine, Aliphatic series secondary amines, such as ethylstearylamine and butylstearylamine; Triethylamine, Aliphatic series tertiary amines, such as trimethylamine, trihexyl amine, and trioctylamine; Triaryl amine, Aliphatic series unsaturation amines, such as oleylamine; Lauryl aniline, As aromatic amine [ such as stearylamine, a triphenylamine, N,N-dimethylamine, and dimethylbenzyl aniline, ], and other amines, Monoethanolamine, diethanolamine, triethanolamine, Dimethylamino ethanol, diethylenetriamine, triethylenetriamine, Tetrahydropeptamine, benzylamine, diethylamino propylamine, Xylylene diamine, ethylenediamine, hexamethylene diamine, Dodecamethylene diamine, dimethyltetlenediamine, triethylbenzenediamine, Guanidine, diphenylguanidine, N,N,N',N'-tetramethyl ethylene diamine, 2,4,6-tris(dimethyl aminomethyl) phenol, Although morpholine, N-methylmorpholine, 2-ethyl-4-methylimidazole, 1, and 8-diazabicyclo (5. 4. 0) undecene 7 (DBU) etc. are mentioned, it is not limited to these.

[0119]

In this invention, an amino group content silane coupling agent can also be used as a (C) ingredient. Said amino group content silane coupling agent is a compound which has a basis (henceforth a hydrolytic silicon group) and an amino group containing a silicon atom which a hydrolytic basis combined. As an example of this hydrolytic silicon group, X can mention a thing which is a hydrolytic basis among bases expressed with a general formula (1). Although a basis already illustrated as a hydrolytic basis can specifically be mentioned, a methoxy group, an ethoxy basis, etc. are preferred from a point of a hydrolysis rate. As for especially the two or more number of a hydrolytic basis, three or more pieces are preferred.

[0120]

As an example of an amino group content silane coupling agent, gamma-aminopropyl trimethoxysilane, gamma-aminopropyl triisopropoxy silane, gamma-aminopropyl trimethoxysilane, gamma-(2-aminoethyl) methyl dimethoxysilane, gamma-(2-aminoethyl) aminopropyl methyl dimethoxysilane, gamma-(2-aminoethyl) aminopropyl trimethoxysilane, gamma-(2-aminoethyl) aminopropyl triisopropoxy silane, gamma-(2-aminoethyl) aminopropyl trimethoxysilane, gamma-(2-aminoethyl) aminopropyl triisopropoxy silane, gamma-(2-aminoethyl) aminopropyl trimethoxysilane, gamma-(2-aminoethyl) aminopropyl trimethoxysilane, gamma-(2-aminoethyl) aminopropyl triisopropoxy silane, gamma-(2-aminoethyl) aminopropyl trimethoxysilane, N-phenyl-gamma-aminopropyl trimethoxysilane, N-benzyl-gamma-aminopropyl trimethoxysilane, N-vinylbenzyl gamma-aminopropyl trimethoxysilane, etc. can be mentioned. Amino modifying silyl polymer which is the denatured derivative, silanizing amino polymer, an unsaturation aminosilane complex, a phenylamino long chain alkyl silane, amino silanizing silicone, etc. can use these. The above-mentioned amino group content silane coupling agent may be used only by one kind, and may carry out two or more kind mixing use.

[0121]

As these (C) ingredients, since co-catalyst ability changes greatly with structure of the (C) ingredient itself, compatibility with the (A) ingredient, etc., it is preferred to choose a compound which was suitable according to a kind of (A) ingredient to be used. For example, when using an isobutylene system polymer as a (A) ingredient, aliphatic series secondary amines, such as comparatively long-chain aliphatic series secondary amines, such as diethyl amine and diisopropyl amine, and

dicyclohexylamine, are preferred from a point that co-catalyst ability is high.

[0122] As for loadings of an amine compound which is the aforementioned (C) ingredient, about 0.01–20 weight sections are preferred to organic polymer 100 weight section of the (A) ingredient, and also its 0.1 – 5 weight section is more preferred. A cure rate may become it slow that loadings of an amine compound are less than 0.01 weight sections, and a hardening reaction becomes fully difficult to advance. On the other hand, if loadings of an amine compound exceed 20 weight sections, pot life may become short too much, and is not preferred from a point of workability.

[0123] Silane coupling agents other than an amino group content silane coupling agent can also be used for a constituent of this invention.

[0124] As functional groups other than an amino group, a sulphydryl group, an epoxy group, a carboxyl group, a vinyl group, an isocyanate group, isocyanurate, halogen, etc. can be illustrated.

[0125] As an example of silane coupling agents other than an amino group content silane coupling agent, gamma-mercaptopropyl triethoxysilane, gamma-mercaptopropyl trimethoxysilane, Sulfhydryl group content Silang, such as gamma-mercaptopropyl(methyl) dimethoxysilane and gamma-mercaptopropyl trimethoxysilane; Gamma-glycidoxypropyl(trimetoxysilane, gamma-glycidoxymethyl trimethoxysilane, gamma-glycidoxypropyl methyltrimethoxysilane, beta-(3, 4-epoxy)clohexyl) trimethoxysilane, Epoxy group content Silang, such as beta-(3,4-epoxy)clohexyl) trimethoxysilane; beta-carboxyethyl triethoxysilane, beta-carboxyethyl phenylbis(2-methoxyethoxy)Silang. Carboxylshanes, such as N-beta-(carboxymethyl) aminoethyl gamma-aminopropyl trimethoxysilane; Vinyltrimethoxysilane, vinyl type unsaturation group content Silang [, such as gamma-oxypropyl methyl dimethoxysilane, vinyl type unsaturation group content Silang [, such as gamma-AKURO yloxy propylmethyl triethoxysilane, ] — containing halogen Silang [, such as gamma-chloropropyl trimethoxysilane, ] — isocyanurate silanes [, such as tris (trimethoxysilyl) isocyanurate, ]. Isocyanate group content Silang, such as gamma-isocyanate propyltrimethoxysilane, gamma-isocyanatepropyl triethoxysilane, gamma-isocyanate propylmethyl diethoxysilane, and gamma-isocyanate propylmethyl dimethoxysilane, can be mentioned. A block isocyanate silane, silanizing polyester, etc. which are the derivatives which denaturalized these can be used as a silane coupling agent.

[0126] The amount of [in case used of using silane coupling agents other than an amino group content silane coupling agent ] has 0.01 – 20 preferred weight section to (A) ingredient 100 weight section, and also its 0.1 – 5 weight section is more preferred.

[0127] Various fillers can be used for a hardenability constituent of this invention if needed. As an example of said filler, for example Wood flour, PARUBU, a cotton chip, Asbestos, glass fiber, carbon fiber, mica, walnut shell powder, chaff powder, Graphite, diatomite, clay, fume silica, sedimentation nature silica, Crystalline silica, fused silica, dolomite, a silicic acid anhydride, carbon black, calcium carbonate, clay, talc, titanium oxide, aluminium hydroxide, magnesium carbonate, aluminum impalpable powder, the Flint powder, the end of zinc dust, etc. are raised. Among these fillers, sedimentation nature silica, fume silica, crystalline silica, fused silica, dolomite, carbon black, calcium carbonate, titanium oxide, talc, etc. are more preferred than points, such as a reinforcing effect, the increase in quantity effect, and an ease of acquisition. These fillers may be used independently and may be used together two or more sorts. The amount of [in case used of using a filler ] has 10 – 1000 preferred weight section to (A) ingredient 100 weight section, and its 50 – 300 weight section is still more preferred.

[0128] In a hardenability constituent of this invention, since elongation of a hardened material can be enlarged or a lot of bulking agents can be mixed if a plasticizer is used, using it together with a bulking agent, it is more effective. As an example of a plasticizer, dioctyl phthalate, dibutyl phthalate, \*\*\* phthalic ester, such as butylbenzyl phthalate, di-isododecyl phthalate, and JIISO undecyl phthalate, Dioctyl adipate. \*\*\* aliphatic dibasic acid ester, such as succinic acid isodecyl and dioctyl

sebacate; Diethylene glycol dibenzozate, \*\*\*\* glycol ester, such as pentaerythritol ester, Butyl oleate, \*\*\* aliphatic series ester species, such as methyl acetyl ricinoleate; Tricresyl phosphate, \*\*\* phosphoric ester, such as triacetyl phosphate and phosphoric acid octyl/diphenyl; Epoxidized soybean oil, \*\*\* epoxy plasticizers, such as epoxidation linseed oil and epoxy stearic acid benzyl; Polyether, such as a polyester plasticizer, polypropylene glycol which is polyester of dibasic acid and dihydric alcohol, and its derivative; [Poly alpha-methylstyrene, ] Polystyrene, such as polystyrene; Polybutadiene, Butadiene Acrylonitrile, polychloroprene, polysoprene, polybutene, hydrogenation polybutadiene, hydrogenation polystyrene, Hydrocarbon system oligomer, such as process oil; chlorinated paraffins are illustrated.

[0129] These plasticizers may be used alone and may be used together two or more sorts. A desirable result will be obtained if the amount of plasticizers is used in the range of one to 200 weight section to reactive-silicon-group-containing-organic-polymer 100 weight section.

[0130] An epoxy resin can be used together in a hardenability constituent of this invention. In this case, an epoxy resin and reactive silicon group containing organic polymer can be reformed.

[0131] As an epoxy resin, can use a publicly known thing widely conventionally, and For example, a bisphenol A type epoxy resin, Fire retardancy type epoxy resins, such as bisphenol F type epoxy resin and glycidyl ether of tetramethylolphenol A, Novolak type epoxy resin, a hydrogenation bisphenol A type epoxy resin, A glycidyl ether type epoxy resin of a bisphenol A propylene oxide addition, Diglycidyl p-oxobenzonic acid, phthalic acid diglycidyl ester, Phthalic acid diglycidyl ester system epoxy resins, such as tetrahydrophthalic acid diglycidyl hexahydrophthalate, m-aminophenol series epoxy resin, a diaminodiphenylmethane system epoxy resin, Urethane modified epoxy resin, various cycloaliphatic-epoxy-resin, N, and N-diglycidyl aniline, N,N-diglycidyl o-toluidine, triglycidyl isocyanurate, An epoxidation thing of unsaturation polymers, such as glycidyl ether of polyhydroic alcohol, such as polyalkylene glycol diglycidyl ether and glycerin, a hydantoin type epoxy resin, and petroleum resin, etc. can be mentioned.

[0132] It is desirable from a point of a thing containing at least two epoxy groups having high reactivity when hardening, and a hardened material tending to form the three-dimensional network structure into a molecule, also in these epoxy resins. As a desirable epoxy resin, a bisphenol A type epoxy resin, bisphenol F type epoxy resin, novolak type epoxy resin, and a phthalic acid diglycidyl ester system epoxy resin can be illustrated from availability and an adhesive point.

[0133] As a hardening agent of an epoxy resin, a publicly known hardening agent for epoxy resins can be used widely conventionally. For example, triethylenetetramine, tetraethylentetramine, diethylamino propylamine, N-aminomethyl piperazine, m-xylylene diamine, m-phenylenediamine, Diamindiphenylmethane, diamindodiphenyl sulfone, isophorondiamine, Amines, such as 2,4,6-tris (dimethyl) aminomethyl phenol, Tertiary amine salts, polyamide resin, ketimines, and aldimine. Insidious hardening agents, such as enamines, imidazole derivatives, and dicyandiamides. Boron trifluoride complex compounds, phthalic anhydride, hexahydro phthalic anhydride, Anthydrous carboxylic acid, such as tetrahydro phthalic anhydride and methylene tetrahydro phthalic anhydride, a DODESHINIRU succinic anhydride, Pyromellitic dianhydride, and anhydrous KUOREN acid, alcohols, phenols, and carboxylic acid can be mentioned.

[0134] An epoxy resin receives reactive-silicon-group-containing-organic-polymer 100 weight section, it is preferred to use it in the range of one to 100 weight section and also ten to 50 weight section, and it is preferred to blend a hardening agent of an epoxy resin per epoxy resin 100 weight section in the range of one to 200 weight section and also ten to 100 weight section.

[0135] An ingredient which limitation in particular does not have in the method of preparation of a hardenability constituent of this invention, for example, was described above is blended, it kneads under ordinary temperature or heating using a mixer, a roll, a kneader, etc., or an ingredient is dissolved using a little suitable solvents, and a usual method of mixing may be adopted. A I liquid

type, two-component type, or many liquid type compound can also be built and used by combining these ingredients suitably.

[0136]

If a hardenability constituent of this invention is exposed into the atmosphere, by operation of moisture, it will form network structure in three dimensions, and will harden it to a solid which has rubber-like elasticity.

[0137]

In a hardenability constituent of this invention, various additive agents can be added if needed. Other curing catalysts as an example of said additive for example (for example, tetravalent tin, divalent tin, etc.). Adhesive grant agents which adjust the tractive characteristics of a hardened material to generate, such as a physical-properties regulator and a silane coupling agent, An antioxidant, radical inhibitor, an ultraviolet ray absorbent, a metal deactivator, anti-ozoneant, light stabilizer, the Lynn system peroxide decomposition agent, lubricant, paints, a foaming agent, a photo-setting resin, a thixotropic grant agent, etc. are raised.

[0138]

An example of such an additive is indicated in each gazette of JP4-69659,B, JP,7-108928,B, JP,63-254149,A, and JP,64-22904,A, for example.

[0139]

Since a hardenability constituent of this invention has outstanding weatherability, heat resistance, water resisting property, and electric insulation resulting from a principal chain skeleton and it has high intensity and a physical-properties improvement effect of high elongation. It can use conveniently for electrical insulation materials, such as electric electronic component materials, such as a structural elastic sealing compound, a sealing material for multiple glass, a solar cell rear-face sealing agent, pre-insulation an electric wire, material for cables, a binder, adhesives, a paint, infusion, a coating material, a sealing agent for rust prevention / water proof, etc. It is useful especially when used for adhesives, a structural elastic sealing compound, or a sealing material for siding.

[Example]

[0140] Although working example and a comparative example explain this invention concretely below, this invention is not limited to this.

[0141]

(Working example 1-4, comparative example 1)

(A) As opposed to isobutylene system polymer (Kaneka Corp. make, trade name EPP05S;isobutylene system polymer / paraffin series process oil = 100/50) 150 weight section which has a reactive silicon group as an ingredient, Epoxy resin (product [ made from Oil recovery Shell Epoxy ], trade name Epicoat 828) 5 weight section, Hydrogenation alpha-olefin oligomer (product [ made from Idemitsu Petrochemistry ], trade name FAO5004) 60 weight section, Colloid calcium carbonate (Maruo Calcium Co., Ltd. make, trade name SHIRETTI SU 200) 50 weight section, Colloid calcium carbonate (product [ made from Shiroishi Calcium ], trade name SOFUTON 320) 40 weight section, Photo-setting resin (Toagosei make, trade name ARONIKKUSU M-309) 3 weight section, Benzotriazol system ultraviolet ray absorbent (Ciba-Geigy Japan make, trade name tironivin 327) 1 weight section, Hindered amine light stabiliser (Sankyo Co., Ltd. make, trade name SANORU LS-770) 1 weight section, hindered phenolic antioxidant (Ciba-Geigy Japan make, trade name IRUGA NOX 1010) 1 weight section, and water 5 weight section were measured respectively, and it often kneaded with a 3 paint roll, and was considered as base resin.

[0142]

next — as the (B) ingredient — octyllic acid (2-ethylhexanoic acid) calcium salt (the Nihon Kagaku Sangyo Co., Ltd. make.) The trade name NIKKAOOKU Chicks Ca 5% toluene solution was used as a hardening agent [ in / for the thing for which diisostyrene amine (the Kao Corp. make, Firmin D86) is respectively shown in Table 1 as a (C) ingredient and which could number/ of weight sections / measure, could use the spatula, and was stirred and mixed / working example 1 ].

[0143]

here — as the (B) ingredient of this invention — naphthenic acid vanadium (the Nihon Kagaku Sangyo Co., Ltd. make.) as a trade name NIKKANAFU textile V 2% toluene solution and the (C)

ingredient — diisostyrene (the Kao Corp. make.) The number[ of weight sections ]—used thing which shows Firmin D86 in Table 1 respectively is made into working example 2, (B) as an ingredient — octyllic acid (2-ethylhexanoic acid) iron (the Nihon Kagaku Sangyo Co., Ltd. make.) The number[ of weight sections ]—used thing which shows respectively lauryl amine (made by Wako Pure Chemical Industries, Ltd.) in Table 1 as a trade name NIKKAOOKU Chicks Fe 6% toluene solution and a (C) ingredient is made into working example 3. The number[ of weight sections ]—used thing which further more shows respectively lauryl amine (made by Wako Pure Chemical Industries, Ltd.) in Table 1 as a (B) ingredient as octyllic acid (2-ethylhexanoic acid) titanium (3% toluene solution) and a (C) ingredient was made into working example 4. On the other hand, the number[ of weight sections ]—used thing which shows lauryl amine in Table 1 respectively as (B) octyllic acid (2-ethylhexanoic acid) tin (Japanese east transformation Make, trade name neo SUTAN U-28) and a (C) ingredient was made into the comparative example 1.

[0144]

These base resin and hardening agents were mixed by the ratio shown in Table 1, respectively, and what constructed the aluminum base material to H type in accordance with the manufacturing method of the tensile adhesive property specimen to which this is specified JIS A5758-1992 was filled up. Care-of-health conditions were made into 23 \*\*x 7 +50 \*\*x seven days. [ per day ] The used aluminum uses the alumite treatment aluminum of 50x50x5-mm size based on JIS H4000 as a substrate. After purifying by methyl ethyl ketone (made by Wako Pure Chemical Industries, Ltd.) before being filled up with the compound, the primer (the Toray Industries Dow Corning make, trade name D-2) was dried and used under ordinary temperature for spreading and 30 minutes.

[0145]

In accordance with the tensile cement test method of 5758 - 1992 N of JIS A, the examination was presented with H type sample obtained by the above-mentioned method on condition of speed-of-testing 50 mm/min among 23 \*\*, and the thermostatic chamber of 50\*\*5% of humidity.

[0146]

The recovery was measured by the following methods. First, after making H type sample which ended the above-mentioned care of health immersed into 50 \*\* warm water for one day and taking it out, it was neglected under the room temperature on the 1st. Subsequently, after having compressed and fixed to 70% so that sample thickness might be set to 12 ~ 8.4 mm, and heating a sample in 100 \*\* hot air drying equipment for one day, it released from compression and was neglected under the room temperature on the 1st. The thickness of the sample in this case was measured and the recovery to a compressed part was computed.

[0147]

Time (leather-covered time) until it fills the same compound in an ointment can simultaneously as a measure which estimates hardenability and stretches a hide on the surface under 23 \*\* and the conditions of 50% of relative humidity was measured. The one where leather-covered time is shorter shows that hardenability is high.

[0148]

A result is shown in Table 1. The filled hardened material is that cohesive failure is shown, and CF showing the fracture state in front is a fracture state which can be searched for as a sealing material.

[0149]

[Table 1]

		聚丙烯		聚丙烯		聚丙烯		聚丙烯	
(A) 成分		EPG054		EPG054		EPG054		EPG054	
主 剂	PA0504	phr	phr	phr	phr	phr	phr	phr	phr
	沙177200								
	沙173200								
	MC-5								
	EP-1-1878								
塑 料	7113-AK-M-300								
	1MA-1021010								
	环化-2327								
	热-MLS-710								
	水								
塑 化 剂	(B) 成分	沙173200 沙173200 沙173200 沙173200 沙173200		phr	phr	phr	phr	phr	phr
	沙173200	沙173200 沙173200 沙173200 沙173200 沙173200		phr	phr	phr	phr	phr	phr
	沙173200	沙173200 沙173200 沙173200 沙173200 沙173200		phr	phr	phr	phr	phr	phr
	沙173200	沙173200 沙173200 沙173200 沙173200 沙173200		phr	phr	phr	phr	phr	phr
	沙173200	沙173200 沙173200 沙173200 沙173200 沙173200		phr	phr	phr	phr	phr	phr
特 性 性	(C) 成分	沙173200 沙173200 沙173200 沙173200 沙173200		phr	phr	phr	phr	phr	phr
	沙173200	沙173200 沙173200 沙173200 沙173200 沙173200		phr	phr	phr	phr	phr	phr
	沙173200	沙173200 沙173200 沙173200 沙173200 沙173200		phr	phr	phr	phr	phr	phr
	沙173200	沙173200 沙173200 沙173200 沙173200 沙173200		phr	phr	phr	phr	phr	phr
	沙173200	沙173200 沙173200 沙173200 沙173200 沙173200		phr	phr	phr	phr	phr	phr
物理特性		拉伸强度 MPa		拉伸强度 MPa		拉伸强度 MPa		拉伸强度 MPa	
H型塑料特性		5.0		0.06		0.07		0.08	
拉伸强度		拉伸强度 %		0.46		0.64		0.27	
拉伸强度 %		710		760		440		580	
拉伸强度 %		CP		CP		CP		CP	
拉伸强度 %		73		73		73		73	
拉伸强度 %		27		27		27		27	
拉伸强度 %		29		29		29		29	
拉伸强度 %		4		4		4		4	
拉伸强度 %		3		3		3		3	
拉伸强度 %		0.1		0.1		0.1		0.1	
拉伸强度 %		0.36		0.34		0.34		0.34	
拉伸强度 %		310		310		310		310	
拉伸强度 %		CP		CP		CP		CP	
拉伸强度 %		29		29		29		29	

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[0150] Using an isobutylene system polymer as an ingredient (A) as shown in Table 1 as a (B) ingredient, When distearyl amine and lauryl amine were used together for octylic acid calcium, naphthenic acid vanadium, and octylic acid titanium as a co-catalyst (working example 1, 2, and 4), the leather-covered time about equivalent has been secured as compared with the case where octyl tin and lauryl amine of the comparative example 1 are used together. On the other hand, in the case (working example 3) where used octylic acid iron as a (B) ingredient, and lauryl amine is used as a co-catalyst, although it had been 9 hours or more leather-covered time, one day afterward, it checked having hardened enough. The hardened material which was obtained also in the gap to use such carboxylic acid metal salt for (working example 1-4) showed breaking strength with high all, and elongation after fracture to the comparative example 1 which used octylic acid tin and lauryl amine. About stability, although the recovery at the time of using octylic acid titanium and octylic acid iron was lower than the comparative example 1, all had stability. High stability was shown when especially

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(Working example 5, comparative example 2)

(A) As a polyether system polymer which has reactant silicon as an ingredient, As opposed to MS polymer S203 (made by Kaneka Corp.) 95 weight section, plasticizer (trade name PP-G-3000) 55 weight section and a dripping inhibitor (made in Kusumoto Chemicals.) The amount part of trade name DISUPARON #6000 duplex, benzotriazol system ultraviolet ray absorber (Giba-Geigy, Japan make, trade name tinuvin 327) 1 weight section, and hindered amine light stabilizer (Sankyo Co., Ltd. make, trade name SANORU LS-770) 1 weight section were measured, and it mixed in \*\*\*\*\*, the colloid calcium carbonate (the product made from Shiraishi Industry,) which dried this by decompression stirring at 120  $\times$  with 5L planetary mixer beforehand for 2 hours It mixed to trade name Hakuenuka CCR120 weight section and titanium oxide (Ishihara Sangyo Kaisha, Ltd. make, trade name TIPACU R-820) 20 weight section, and stirring mixing was carried out for 10 minutes. Took out the mixture, and it kneaded once with 3 paint roll, and also checked that dried by decompression stirring at 120 for 2 hours, and water content decreased to about 700 ppm with 5L planetary mixer again. After cooling a mixture, it added and stirring mixing of the amount part of dehydrator (Nippon Unicar make, trade name A-171) duplex was carried out for 15 minutes. Next, it added and stirring mixing of the aminosilane coupling agent (Nippon Unicar make, trade name A-1120) 3 weight section was carried out for 15 minutes. The octylic acid zirconium (the Nihon Kagaku Sangyo Co., Ltd. make, trade name NIKKOKU Chicks Zr/2% toluene solution) which is the (B) ingredient adjusted further beforehand.

(C) The number of weight sections which shows lauryl amine (made by Wako Pure Chem) which is a diamine. Table 2 showed this was obtained.

performed for 5 minutes. The cartridge made of paper (product made from the Showa round cylinder) by which the coat was carried out was filled up with the aluminum for 1 liquid so that the obtained mixture might not involve in a bubble, and 1 liquid mold-curing nature constituent was obtained. What used the amount part of dibutyltin diacetate (Japanese east transformation Make, trade names U-220) duplex was made into the comparative example 2 instead of the mixture of said octylic acid zirconium and lauryl amine.

[0152] After neglecting the above-mentioned 1 liquid mold-curing nature constituent under a room temperature for 24 hours or more, the specimen used for a tensile test was produced as follows. What constructed the aluminum base material to H type in accordance with the manufacturing method of the tensile adhesive property specimen specified to JIS A5738-1992 using the cancer marketing of 1 liquid mold-curing nature constituent from 1 liquid cartridge was filled up. Care-of-marketing conditions were made into 23 \*\*x14+50 \*\*x14 days. [ per cartridg ] Using the alumite substrate of the 50x50x5-mm size based on JIS H4000, before the aluminum used as a substrate filled up with the compound, it was purified by methyl ethyl ketone (made by Wako Pure Chemical Industries, Ltd.). In accordance with the tensile cement test method of 5758 - 1992 N of JIS A, the examination was presented with H type sample obtained by the above-mentioned method on condition of for 23 \*\*\*, and humidity 50 inside of \*\*5% of thermostatic chamber and spread-of-test [ of 50 mm ]. The hardened material set stress when it elongated 150% to M50, M100, and M150, 100% 50%, respectively, and set TB and elongation at the time of a fracture to EB for the stress the time of a fracture.

Since an adhesive property turned into the important characteristic as a liquid mold-curing nature constituent, the adhesive property was checked using anodized aluminium and a vinyl chloride steel plate. On each substrate which purified the surface by methyl ethyl ketone, 1 liquid mold-curing nature constituent was placed from 1 liquid cartridge using commercial cancer to the crest shape with a 1 cm<sup>[1] in width] x length of about 3 cm, and it was recuperated for 23 \*\*\*x 14 +50 \* 14 days per day. The manual friction test was done after care of health, cutting an adhesion side deeply with a cutter knife, and the surface of the substrate was observed. The filled hardened material is that cohesive failure is shown, and CF in Table 2 is a fracture state searched for as a sealing material. [0153]</sup>

Depths hardenability took out the portion which has hardened the surface which filled in the 80-mm-long polyethylene tube 1 liquid mold-curing nature constituent produced in working example 5, and was made at the tip of a tube in it at 16.5 mm in inside diameter on the day which the days to

In order to check the practicality as a liquid mold-curing nature constituent, where 1 liquid cartridge is filled up with a constituent, it stored for two weeks in the hot air drying equipment which carried out the temperature control to 50 \*\*, and the depths hardenability after storage was measured visually, and measured the hardened thickness with slide calipers.

[0156]

and it kneaded once with 3 paint roll, and also checked that dried by decompression stirring at 120 °C for 2 hours, and water content decreased to about 700 ppm with 5L planetary mixer again. After cooling a mixture, it added and stirring mixing of the amount part of dehydrator (Nippon Unicar make, trade name A-71) duplex was carried out for 15 minutes. Next, it added and stirring mixing of the aminosilane coupling agent (Nippon Unicar make, trade name A-1120) 3 weight section was carried out for 15 minutes. The octylic acid zirconium (the Nikon Kagaku Sangyo Co., Ltd. make, trade name NIKKAOOKU Chicks Zr-12% toluene solution) which is the (B) ingredient adjusted further beforehand, (C) The number of weight sections which shows lauryl amine (made by Wako Pure Chem.) which is an

http://www.iowl.com/industry/semiconductors/semiconductor-industry-analysis-report-2010-05-06

[9157]

[0157] As opposed to the polyether system polymer which serves as the (A) ingredient of this invention in working example 5, (B) By using the lauryl amine which acts the carboxylic acid zirconium salt which acts as a co-catalyst as a (C) ingredient further as a silanol condensation catalyst as an ingredient, Although hardenability was slightly inferior as compared with the comparative example 2 using dibutyltin diacetate as a tetravalent tin catalyst, almost comparable elongation and an adhesive property were revealed and it checked that 1 liquid mold-curing nature constituent which may be sufficient for practical use was obtained [Table 2].

[0158]

(Synthetic example 1) Use polyoxypolypropylene triol of the molecular weight 3,000 [about ] as an initiator, and propylene oxide is polymerized in a zinc hexa cyanocobaltate glyme complex compound catalyst. Number average molecular weight about 26,000 (polystyrene reduced molecular weight in which the column measured the solvent using the TOSOH TSK-GEL H type using TOSOH HLC-8120GPC as a liquid-sending system) polypropylene oxide was obtained. Then, the methanol solution of NaOME of the equivalent was added 1.2 times to the hydroxyl group of this hydroxyl group end polypropylene oxide, and methanol was distilled off, and also the allyl chloride was added, and the hydroxyl group of the end was changed into the allyl group. By the above, the end obtained 3 organic-functions polypropylene oxide of the number average molecular weight 26,000 [about ] which is an allyl group.

[9159] The nitrogen purge was carried out, after having added 500 g of allyl end 3 organic-functions polypropylene oxide and 10 g of hexane which were obtained above to 1L autoclave, dehydrating azotropically at 90 °C and distilling off hexane under decompression. On the other hand, after adding 30 micro of platinum divinyl dilistoxane complex (it is 3% of the weight of xylene solution by platinum conversion) 1, 70 g of dimethoxymethylsilane was dropped. After making the mixed solution react at 90 °C for 2 hours, unreacted dimethoxymethylsilane was distilled off under decompression and the reactive silicon group content polyoxalkylene series polymer ( $A-1$ ) was obtained. The number average molecular weight of the obtained polymer ( $A-1$ ) was about 26,000. The silyl group introduction rate was measured by the following methods by  $^1\text{H-NMR}$  (it measures in a  $\text{CDCl}_3$  solvent using  $[\text{EO}] = [\text{N}-A400]$ .

[0160] -Receive the peak integral value of  $\text{CH}_3$  group (near 1.2 ppm) of the polypropylene oxide main chain of said allyl end 3 organic-functions polypropylene oxide before a hydrosilylation reaction. Relative value of the peak integral value of an allyl end proton (near  $\text{CH}_2=\text{CH}-\text{CH}_2$ , -5.1 ppm) : <1>. Receive the peak integral value of  $\text{CH}_3$  group (near 1.2 ppm) of the polypropylene oxide main chain of the silylethoxy end 3 organic-functions polypropylene oxide before a hydrosilylation reaction.

end polypropylene oxide ( $A_1^-$ ) after a hydroxylation reaction. Relative-value:  $\langle 2 \rangle$  of the peak integrated value of the proton (near  $\text{CH}_3(\text{CH}_2\text{O})_2\text{Si}-\text{CH}_2-\text{CH}_2^{\sim}0.6$  ppm) of the methylene group combined with the silicon atom of the end silyl group to the silyl group introduction rate  $\langle 2 \rangle/\langle 1 \rangle$  was 78%.  
Fig. 1c-11

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**Synthetic example 2**  
After attaching a three-way cock to the resisting pressure glass container of 2L and carrying out the nitrogen purge of the inside of a container to it. Using an injector, in a container 262.5 ml of ethylcyclohexane (thing dry) by neglecting 1 or more night with the molecular sieves 3A), and 787.5 ml of toluene (thing dry by neglecting 1 or more night with the molecular sieves 3A), p-DCC (the following compound 1A) 350 mg (0.1 mmol) was added.

newer compounds ( $n = 4-5$ ) were also found to contain a 1,3-dihydro-2H-pyrazole ring system.

[Formula 10]

(A)

[0163] Next, the resisting pressure glass liquefied gas extraction pipe with a needle valve containing 436 ml (5.15 mol) of isobutylene monomers was connected to the three-way cock, and after attaching the polymerization vessel all over dry ice / ethanol bus of -70 °C and cooling, the inside of a container was made decompression using the vacuum pump. After opening the needle valve and introducing an isobutylene monomer in a polymerization vessel to a liquefied gas extraction pipe, the inside of a container was returned to ordinary pressure by introducing nitrogen from one side in a three-way cock. Next, 0.72 g (7.7mmol) of 2-methylpyridine was added. Next, 10.58 ml (96.5mmol) of titanium tetrachloride was added, and the polymerization was started. 70 minutes after the polymerization start, 7.20 g (63.0mmol) of allyl trimethylsilane was added, and the introduction reaction of the allyl group was performed to molecular chain terminals. After adding allyl trimethylsilane and 200 ml of water washed [120 minutes], the reaction solution 4 times, the allyl end isobutylene system polymer obtained.

[0164] was obtained by dissolving oil & solvent.

Subsequently, the allyl end isobutyl/ene system polymer 200g obtained in this way, the paraffin-base process oil (the Idemitsu Kosan make.) which is a hydrocarbon system plasticizer After mixing trade name Diana process PS-32 100g and carrying out temperature up to about 75 \*\*, the  $7.5 \times 10^{-5}$  equivalent was added [ methyl dimethoxysilane ] for 2.4 Eq and a platinum (vinyl siloxane) complex to the allyl group of an end to the allyl group of an end, and the hydrosilylation reaction was performed FT-IR (Shimadzu IR-408) performed reaction pursuit, and the absorption based on the olefin of 1640

$\text{cm}^{-1}$  disappeared in about 20 hours.

[0165] 2/1 of PS-32 which is the isobutylene system polymer and plasticizer which have a reactive silicon group in the both ends of the target chain of the mixtures (A-2) of the weight ratio were obtained.

[0166] In this way, if the obtained polymer is measured by the GPC method (it was considered as the liquid-sending system and, as for the solvent, the column used  $\text{CHCl}_3$  using Shodex K-804 using LC Module 1 made from Waters). The number average molecular weight was 17,600 and  $M_w/M_n$  (ratio of weight average molecular weight to a number average molecular weight) was 1.23.  $^1\text{H-NMR}$  (using *Vincent Cominano*) The proton which belongs to each structure, by measurement in  $\text{CDCl}_3$  (the proton *Vincent Cominano*). The proton which belongs to each structure, by measurement in  $\text{CDCl}_3$  (the proton *Vincent Cominano*).

varian GeminiPro, the proton which belongs to each carbon of initiator origin: 6.5–7.5 ppm) The methyl proton combined with the silicon atom of polymer-terminal origin: As a result of measuring and measuring the intensity of 0.0–0.1 ppm and the resonance signal of methoxy proton 3.4 – 3.5, the end silyl functional group number  $F_n$  (number of the silyl group per

(Working example 6-15, comparative example 3)  
one molecule of isobutylene polymer) was 1.76.  
[0167]

(A) As an ingredient, various additive agents were measured, respectively, and it often kneaded with

3 paint roll according to the formula shown in Table 2, using the reactive silicon group content polyoxalkylene series polymer (A-1) obtained in the synthetic example 1, and was considered as base resin.

[0168]. Next, as a (B) ingredient which is a silanol condensation catalyst, lauryl amine was further measured for the various carboxylic acid metal salt shown in Table 1 to the above-mentioned bases resin as a (C) ingredient, the spatula was used for it, and it stirred and mixed for 3 minutes. It was made for all the numbers of mole of the metal atom containing the number of addition parts of the various carboxylic acid metal salt of the (B) ingredient to become the same here.

[0169] The mold about 3 mm thick was used and filled up with the spatula after mixing, and care of health on 23-#\*x3+50 #\*\* the 4th was performed. [ per day ] From the obtained hardened material sheet, the No. 3 type dumbbell specimen specified to JIS K 6301 was pierced, and the tensile test was carried out in the autograph (tension speed 200 mm/min). The modulus (M50) in the time of being extended 50%, the intensity at the time of a dumbbell fracture (Tb), and the elongation at the time of a dumbbell fracture (Eb) were measured.

[0170] The combination presentation of base resin, a curing catalyst, etc. and the physical—properties

Evaluation  
[0171]

The mold about 3 mm thick was used and filled up with the spatula after mixing, and care of health on 23 \*x3+50 \*\*x the 4th was performed. [ par day ] From the obtained hardened material sheet, the No. 3 type dumbbell specimen specified to JIS K 6301 was pierced, and the tensile test was carried out in the autograph (tension speed 200 mm/min). The modulus (M50) in the time of being extended 50%, the intensity at the time of a dumbbell fracture ( $T_b$ ), and the elongation at the time of a

The combination presentation of base resin, a curing catalyst, etc. and the physical-properties of the hardened material obtained from it are shown in Table 3.

Evaluation  
[0171]

http://www.todlinit.go.jp/cgi-bin/tran.web.cgi.cgi?atw.u=http://3A%2Fwww4.ipd[...]

[017]

When the various carboxylic acid metal salt of working example 6-15 is used compared with the comparative example 3 using 2-ethylhexanoic acid tin as a silanol condensation catalyst as shown in Table 4.

Table 3, the value of  $T_b$  (breaking strength) and  $E_b$  (elongation after fracture) of hardened material physical properties is larger. High elongation and high intensity were shown.

[0173] (Working example 16-28 comparative example 4)

(working example 1-20), comparative example 4/  
(A) Using the mixture (A-2) of the isobutylene system polymer and plasticizer which have as an ingredient the reactive silicon group obtained in the synthetic example 2, various additive agents were measured, respectively, and it often kneaded with a 3 paint roll according to the formula shown in Table 4, and was considered as base resin.

[0174] Next, the various carboxylic acid metal salt shown in Table 4 as a (B) ingredient which is a silanol condensation catalyst was measured, and also as a (C) ingredient, lauryl amine was used together to the above-mentioned base resin, the spatula was used by working example 16-28 and the comparative example 4 for it, and it stirred and mixed for 3 minutes to it. It was recuperated at 23 °F after mixing, and the surface hardened state was evaluated five days afterward. It was made for all the numbers of moles of the metal atom containing the number of addition parts of the various carboxylic acid metal salt of the (B) ingredient to become the same here.

[0175]

The evaluation result of the hardened state five days after the combination presentation of base resin, a curing catalyst, etc. is shown in Table 4. What the surface had hardened O in front for five days afterward is shown, and it is shown that x had not hardened five days after.

[0176]

[0177] When the various carboxylic acid metal salt of working example 16-28 is used as shown in Table 4, in spite of having used the silanol condensation catalyst of the non-tin series, the surface has hardened in five days.

Practical hardenability was shown.

On the other hand, when the carboxylic acid zinc of the comparative example 4 was used, hardenability had not hardened five days after bad.

[0178] As mentioned above, the organic polymer which has at least one reactive silicon group in the (A) molecule, (B) Carboxylic acid calcium, carboxylic acid vanadium, carboxylic acid iron, Carboxylic acid titanium, carboxylic acid potassium, carboxylic acid barium, Carboxylic acid manganese, carboxylic acid nickel, carboxylic acid cobalt, one or more sorts of carboxylic acid metal salt chosen from a carboxylic acid zirconium, and a hardenability [ \*\* and others ] constituent, In spite of being a non-tin series catalyst, practical hardenability is shown, and it turns out that hardened material physical properties are also fitness (high elongation and high intensity).

[0179] (Constituent using the trimethoxysilyl group as a reactive silicon group)

If a trimethoxysilyl group uses the polyoxyalkylene series polymer which exists in molecular chain terminals as a reactive silicon group, a cure rate will become large from the polymer of the synthetic example 1. The direction of a trimethoxysilyl group of this is because reactivity is larger than a methyl dimethoxy silyl group. Such a polymer is indicated to JP,H11-12480,A or JP,2001-72855,A. For example, the same hardenability constituent as working example 6-15 can be prepared using the polymer indicated for the example 1 of manufacture of JP,H11-12480,A. The tack free time of this constituent is shorter than working example 6-15.

[0180] The same hardenability constituent as working example 6-15 can be prepared using the polymer indicated for the example 1-4 of manufature of JP,2001-72855,A. The tack free time of this constituent is shorter than working example 6-15. Therefore, a catalyst amount can be lessened, if cure time is made into the same grade and the polymer which has the above-mentioned trimethoxysilyl group will be used.

[0181] If the mixture of the polymer which has a trimethoxysilyl group, and the polymer which has a methyl dimethoxy silyl group is used as a polymer, cure time and the physical properties of a hardened material are freely controllable. For example, the hardenability constituent of working example 6-15 can be prepared using the polymer which mixed the polymer which has a trimethoxysilyl group, and the polymer which has a methyl dimethoxy silyl group by the weight ratio of 1:10-10:1.

[0182] Working example when the polymer which has a trimethoxysilyl group is used is shown below.

[0183] (Synthetic example 3)

The inside of bottom of  $N_2$  atmosphere 1L autoclave. According to a composite metal complex compound catalyst. It polymerizes. The obtained polypropylene oxide. Use and to the compound number average molecular weight 17,000 and the polyoxypropylene diol 1000g of molecular-weight-distribution  $M_w/M_n=120$  as 19g of gamma-isocyanate propyltrimethoxysilane (Nippon Unicar make Y-5187), and a catalyst. 0.05 g of dibutyl tin screw isooctylthioacetate (made in [ U-360 ] transformation [ Japanese east ]) is added. It reacted at 90 °C until the isocyanate group was no longer detected in IR under the nitrogen air current in this, and the reactive silicon group content polyoxypropylene (A-3) by which the trimethoxysilyl group was introduced into about 80% of ends was obtained.

[0184] (Working example 29-32)

(A) The polyoxyalkylene series polymer (A-1) which has as an ingredient the methyl dimethoxy silyl group obtained in the synthetic example 1, The various carboxylic acid metal salt which is the (B) ingredients according to the formula shown in Table 5 using the polyoxyalkylene series polymer (A-3) which has the trimethoxysilyl group obtained in the synthetic example 3, (C) Lauryl amine which is an

[0177] ingredient was measured, respectively, the spatula was used, and it stirred and mixed for 30 seconds. It was made for all the numbers of mols of the metal atom containing the number of addition parts of the various carboxylic acid metal salt of the (B) ingredient to become almost the same here. The surface was lightly pressed down with the spatula after mixing, and time (leather-covered time) until a constituent stops adhering at the tip of a spatula was measured. An evaluation result is shown in [0185].

Table 5  
[Table 5]

(A) 成分	組成 (重量部)	■塗装		
		29	30	31
(A) 成分	A-1	100	100	100
(B) 成分	ニッケルチオカーボネート(1) (日本化学会塗装標準試験用)	5.6	6.6	5.6
(C) 成分	ニッケルチオカーボネート(1) (日本化学会塗装標準試験用) ラウリルアミン 底塗り時間 (23°C)	0.66	0.66	0.66
		41.91%	21.91%	30.01%

(1) : 2-エチルヘキサノ酸ジカルボン酸のミネラルスピリット溶液、金具(Fe) 含有量 : 6%

(2) : 2-エチルヘキサノ酸カルボン酸のミネラルスピリット溶液、金具(Cu) 含有量 : 5 %

[0186] As shown in Table 5, the polyoxyalkylene series polymer (A-3; working example 30 and 32) which has a trimethoxysilyl group had the cure rate quicker than the polyoxyalkylene series polymer (A-1); working example 29 and 31) which has a methyl dimethoxy silyl group.

[0187]

The same hardenability constituent as working example 6-15 can be prepared using the polyoxyalkylene series polymer (A-3) which has the trimethoxysilyl group obtained in the synthetic example 3. The tack free time of this constituent has short cure time, and good physical properties are acquired.

[0188]

(Constituent which used the epoxy resin together)  
The same hardenability constituent as working example 6-15 can be prepared using the constituent which used together reactive silicon group containing organic polymer and an epoxy resin. When this constituent is used, the manifestation of adhesive strength is quick.  
[Industrial applicability]  
[0189]

(A) The organic polymer which has the hydroxyl group or hydrolytic basis combined with the silicon atom, and has at least one silicon content group which can construct a bridge by forming a siloxane bond, (B) Carboxylic acid calcium, carboxylic acid vanadium, carboxylic acid iron, Carboxylic acid titanium, carboxylic acid potassium, carboxylic acid barium, The hardenability constituent containing one or more sorts of carboxylic acid metal salt which it comes to choose out of carboxylic acid manganese, carboxylic acid nickel, carboxylic acid cobalt, and a carboxylic acid zirconium, While revealing practical hardenability and stability, the hardened material obtained shows the outstanding mechanical physical property which has high intensity and high elongation as compared with the case where the carboxylic acid tin currently used conventionally is used as a curing catalyst. Therefore, the hardenability constituent of this invention is very useful as various elastomers, such as a sealing material, adhesives, a binder.

[Translation done.]